TITLE: **RESIDUES FROM COAL CONVERSION AND UTILIZATION: ADVANCED MINERALOGICAL CHARACTERIZATION AND DISPOSED BY-PRODUCT DIAGENESIS**

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ABSTRACT

OBJECTIVES

The goal of the project is to learn more about the phenomenon of coal conversion by-product (CCB) diagenesis, first described by our group and co-workers at UND EERC seven years ago. CCB diagenesis is a change over time in the mineralogy that occurs after some CCBs are disposed in a landfill or utilized for a civil engineering application. Regulatory environmental tests and civil engineering tests are typically performed on as-generated CCBs, or on CCBs hydrated and cured for relatively short periods such as 7 or 28 days. One would like to know whether the results of these short-term tests will be valid years later. A change in mineralogy is typically accompanied by a gain, loss or redistribution of major, minor and trace elements, and alteration of physical properties. To attain this goal, two objectives were defined:

1. to develop improved methodology for quantitating mineralogy of these complex crystalline phase assemblages, and
2. to investigate the phenomenon of CCB diagenesis further by studying additional materials recovered from disposal landfills or civil engineering works.

ACCOMPLISHMENTS TO DATE

Hydrated CCBs are chemically and mineralogically complex, which makes quantitative mineralogy determination by conventional X-ray diffraction unusable or unreliable. The whole-pattern Rietveld quantitative X-ray diffraction (RQXRD) method, however, can overcome many of the problems and seems well suited to improve reliability. The Rietveld Method uses the whole diffraction pattern to model the parameters that control peak position, peak intensity and peak and background shape: (1) Bragg

diffraction position and intensity which are a function of crystal structure and chemical composition, (2) sample (e.g., level of crystalline order) and specimen (e.g., preferred orientation) effects; and (3) instrumental effects. The modeled diffraction profile is least squares fit to the experimental diffraction profile.

The first step in utilizing the Rietveld method is selection of crystal structure data for each crystalline phase in a mixture. Review of the literature and crystallographic databases for the most reliable structures, and testing with the DOE code GSAS were completed in 1997. The downloadable GSAS input data sets are available for use by other analysts at our website [**http://qxrd.chem.ndsu.nodak.edu/ccbs/**]. Several other Rietveld codes were evaluated for CCB analysis, but GSAS was found to be the most robust and applicable software for this application. A GSAS-based RQXRD protocol has been developed, and analytical sensitivity, precision and accuracy have been determined using standard mixtures of NIST Standard Reference Materials (SRMs) and other CCB phases. Relative error determined from the standard mixtures is in the ±10-15 wt% range. The protocols are in use now for characterization of CCB samples obtained for this project. The protocol has also been applied to a group of NIST SRM Fly Ashes.

In a previous project, five types of CCBs disposed in landfills were studied between 1989 and 1994. Diagenesis was observed in three of the five materials. To obtain a more generic understanding of CCB diagenesis, additional materials and different environmental settings are being studied in this project. CCB core materials have been recovered from four sites:

1. Landfill of FGD material from a Midwest utility burning subbituminous coal – up to 5 years old;
2. Landfill of a Class F fly ash from a utility in Kentucky burning bituminous coal [cooperative work with a consortium of entities headed by the USGS] – up to 20 years old;
3. Landfill of Class C fly ash and FGD material from a North Dakota utility burning lignite – up to 20 years old;
4. Road embankment in Indiana constructed with a mixture of CFBC and stoker ash materials – up to 5 years old.

Characterization of core samples from the Kentucky site is complete. Most of these samples showed no indication of diagenesis (as had been expected for a bituminous coal fly ash), but one zone did show apparently diagenetic ettringite. Analyses of the many hundreds of samples from the other three sites are in progress. To date, evidence of diagenesis has been observed in only one of three remaining materials.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAMS

The utilization of coal for energy production results in large quantities of solid by-products (fly ash, scrubber residues, etc.). Appropriate disposal and/or cost-effective and responsible utilization of the coal combustion and flue gas SO_x scrubbing by-products are important components of the coal utilization regulatory environment and economics. Both depend on knowledge of materials behavior on exposure to nature.

PLANS FOR THE COMING YEAR

Incremental improvements in the RQXRD protocol are anticipated over the next year, especially when more is learned (from the SEM/EPMA work still in progress) about the chemical compositions of ettringite group phases and particle sizes. An important spray dryer scrubber phase, hannebachite (calcium sulfite hydrate), is still problematical for RQXRD methods. These improvements can be easily applied later by repeating the refinement of each computer archived sample data set with the improved input information. Preliminary discussions aimed at obtaining materials from additional sites have been underway for several years. Two of the more promising are a mine haulback CCB consisting of a fly ash/wet FGD mixture that

has been disposed at a mine site, and a disposed FBC material. Efforts aimed at finding cooperators who will provide disposed or utilized materials will continue.

ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

Journal Articles and Book Chapters (peer reviewed)

McCarthy, G.J., Butler, R.D., Grier, D.G., Adamek, S.D., Parks, J.A., and Foster, H.J., Long-Term Stability of Disposed Coal Combustion Byproducts, *Fuel.* 76, 697-703 (1997).

Winburn, R.S., Lerach, S.L., Jarabek, B.R., Wisdom, M.A., Grier, D.G., and McCarthy, G.J. Quantitative XRD Analysis of Coal Combustion By-Products by the Rietveld Method. II. Testing with Standard Mixtures, in *Advances in X-ray Analysis*, 41 (in press).

Conference Proceedings

McCarthy, G.J., Grier, D.G., Winburn, R.S., Coal Combustion Byproduct Diagenesis, in *Proc. Second Intern. Ash Utilization Symp.*, (Publ. by the Center for Applied Energy Research, Univ. of Kentucky, Lexington) 8 pp., October, 1997.

Presentations

Winburn, R.S., Grier, D.G. and McCarthy, G.J., Quantitative XRD Analysis of Coal Combustion By-products by the Rietveld Method. I. Structure Data, 46th Annual Denver X-Ray Conference, Steamboat Springs, CO, August, 1997.

McCarthy, G.J., Butler, R.D., Grier, D.G., Adamek, S.D., Parks, J.A., and Foster, H.J., Long-Term Stability of Disposed Coal Combustion Byproducts, 1997 International Ash Utilization Symposium, Lexington, KY, October, 1997.

McCarthy, G.J., Grier, D.G., Jarabek, B.R. and McCarthy, G.J., Diagenesis of High-Sodium Lignite Combustion By-Products and Carbonation of Stored Samples Containing Ettringite, Fall Meeting of the Materials Research Society, Boston, MA, November 1997.

Vilhauer, R.L., Jarabek, B.R., Grier, D.G., Winburn, R.S., and McCarthy, G.J., A Study of Coal Combustion By-Products from Two Landfills Using Quantitative Rietveld Analysis, 215th Meeting, Am. Chem Soc., Dallas TX, March 1998.

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Lerach, S.L., Wisdom, M., Grier, D.G., Winburn, R., and McCarthy, G.J. Quantitative XRD Analysis of Coal Combustion By-Products by the Rietveld Method. 47th Annual Denver X-ray Conference. Colorado Springs, CO. August 3-7, 1998. [Poster Award]

Lerach, S.L., Wisdom, M., McCarthy, G.J., Grier, D.G., Winburn, R., and Walsh, J.J. Quantitative XRD Analysis of Coal Combustion By-Products by the Rietveld Method. 215th Meeting. American Chemical Society, Anaheim, CA. March 20-25, 1999.

Submitted for Future Presentation

Grier, D.G., Wisdom, M.A., Lerach, S.L., Peterson, R.B., Walsh, J.J., Winburn, R.S., and McCarthy, G.J. Toward Improved Quantitative XRD Analysis of Coal Combustion By-Products Through Rietveld QXRD, 48th Annual Denver X-Ray Conference, Steamboat Springs, CO, August, 1999.

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Lerach, S.L, Winburn, R.S., McCarthy, G.J. and Cathcart, J. D., Quantification of Fly Ash Magnetic Separations, 48th Annual Denver X-Ray Conference, Steamboat Springs, CO, August, 1999.

Grier, D.G., Wisdom, M.A., Lerach, S.L., Peterson, R.B., Walsh, J.J., Winburn, R.S., and McCarthy, G.J. Coal Conversion Byproduct Diagenesis II, Third International Ash Utilization Symposium, Lexington, KY, October, 1999.

Students Supported Under This Grant

Ryan S. Winburn, candidate for Ph.D. in Chemistry.

Dean G. Grier, candidate for M.S. in Soil Science, Research Assistant and Co-Principal Investigator.

Bryan R. Jarabek (B.S. Chemistry, May 1998), Jeffrey. J. Walsh (B.S. Geosciences, 1999), Marissa A. Wisdom (Sr., Chemistry), Stephanie L. Lerach (Sr., Chemistry), Renee B. Peterson (So., Chemistry), Patrick Griffin (So., Chemistry), Raquel L. Vilhauer (Fr., Chemistry, now at U. of Maryland). [Undergraduate Research Fellows with outside support, or Research Assistants supported by the grant.]